

Kinetic study of dichlorocyclopropanation of 4-vinyl-1-cyclohexene by a novel multisite phase transfer catalyst

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Abstract

In this work, the dichlorocyclopropanation of 4-vinyl-1-cyclohexene catalyzed by a new novel phase transfer catalyst was carried out in an alkaline solution/chloroform two-phase medium. This new synthesized phase transfer catalyst, 1,4-bis(triethylmethylammonium)benzene dichloride (DC-X), which possesses two-site activity, was obtained from the reaction of α,α' -dichloro-*p*-xylene and triethylamine. This new novel phase transfer catalyst exhibits higher reactivity than those of the other quaternary ammonium salts. The reaction of chloroform and alkali was carried out at the interface to generate dichlorocarbene which can further react with 4-vinyl-1-cyclohexene to produce mono-dichlorocyclopropane and bis-dichlorocyclopropane products. Rational mechanism of the dichlorocyclopropanation is proposed according to the experimental evidence. The reaction follows a pseudo-first-order rate law. Kinetics of the reactions such as: effect of the catalysts, agitation speed, temperature, alkaline concentration, amount of DC-X catalyst, amount of 4-vinyl-1-cyclohexene (reactant) and volume of chloroform (organic solvent) on the reaction rate were investigated in detail. Peculiar phenomenon for the dependence of the reaction rate on the amount of DC-X catalyst is explained satisfactorily.

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1. Introduction

The essential condition for a chemical reaction to take place is the collision of two or more reactant molecules. Therefore, it is difficult to obtain a high reaction rate from the reaction of two immiscible reactants because of limited contact area. In the past, the conventional methods for solving these problems include using a high agitation speed to increase the contact surface area between two phases, using a high temperature to enhance the reaction rate, and using protic or aprotic solvents to increase the miscibility of the two phases. However, these improvements are limited. Furthermore, there are problems of high energy consumption, production of byproducts and difficulty in purification together with environmental pollution. Therefore, the applications of these techniques to industries are constrained. Fortunately, the technique of phase transfer catalysis is em-

ployed to solve the problems of reactions involving two immiscible reactants. Such reaction is dramatically enhanced by adding a small amount of phase transfer catalyst, e.g., quaternary ammonium salt. It is now considered to be one of the most efficient tools in organic synthesis from two or more immiscible solutions [1–3].

The primary purpose of this work is to employ the technique of phase transfer catalysis to synthesize dichlorocarbene and to react with olefin via dichlorocyclopropanation. In the past, the synthesis of dichlorocarbene was a difficult task. In general, dihalocyclopropanes are valuable compounds which can be treated further with sodium to give alkene, reduced to cyclopropane derivatives and converted to other products [4,5]. Doering and Hoffmann [6] employed the reaction of cyclohexene and dichlorocarbene, which was generated from the reaction of chloroform and potassium *t*-butoxide to produce 7,7-dichlorobicyclo[4.1.0]heptane. However, the application of this technique is still limited due to low conversion of reactant, even at extreme reaction conditions. Makosza and Wawrzyniewicz [7] were the first ones to prepare dichlorocyclopropane under phase

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transfer conditions successfully. The reaction is dramatically enhanced by adding a small amount of benzyltriethylammonium chloride (BTEAC), yielding about 70% of dichlorocyclopropane. Since then, the technique of phase transfer catalysis for the generation of dichlorocarbene has been extensively applied by many chemists [8–14].

Much efforts have been devoted to developing new phase transfer catalyst, such as multisite active catalyst [15,16]. In the present work, a novel new phase transfer catalyst (1,4-bis(triethylmethylammonium)benzene chloride, DC-X) was synthesized from the reaction of α,α' -dichloro-*p*-xylene and triethylamine. This new synthesized multisite active quaternary ammonium salt is then employed as the phase transfer catalyst to synthesize dichlorocyclopropane in an alkaline solution/chloroform two-phase medium. Dichlorocarbene is first generated from the reaction of chloroform and alkali compound. Then, dichlorocarbene further reacts with olefin to generate dichlorocyclopropane. The kinetics of synthesizing dichlorocyclopropane from the reaction of olefin and chloroform in an alkaline solution/chloroform two-phase medium were studied in detail.

2. Experimental

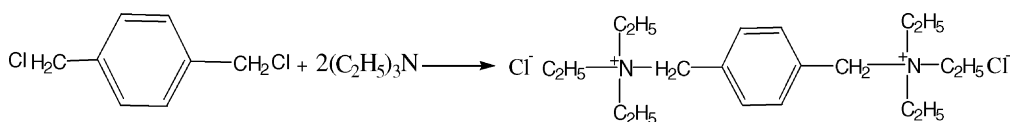
2.1. Materials

All reagents, including 4-vinyl-1-cyclohexene, chloroform, sodium hydroxide, α,α' -dichloro-*p*-xylene, triethylamine, ethanol and nonane and other reagents for synthesis were guaranteed grade (GR) chemicals.

2.2. Procedures

2.2.1. Preparation of two-site active catalyst (DC-X)

Measured quantity of α,α' -dichloro-*p*-xylene (0.01 mol) was introduced into a 150 ml flask. Triethylamine in excess amount dissolving in ethanol (30 ml) was then introduced in the flask for reaction with α,α' -dichloro-*p*-xylene under agitation speed 800 rpm at 60 °C for 24 h. Organic solvent (ethanol) and triethylamine were stripped in a vacuum evaporator. White precipitates of 1,4-bis(triethylmethylammonium)benzene dichloride (DC-X) were obtained. A white solid crystal of the product is obtained by recrystallizing the precipitate in an ethanol solvent.



Similarly, 1,4-bis(triethylmethylammonium)benzene dibromide (DB-X) was obtained from the reaction of α,α' -dibromo-*p*-xylene and triethylamine.

2.2.2. Synthesis of products (mono-dichlorocyclopropane and bis-dichloro-cyclopropane)

Measured quantities of NaOH (8 g) and DC-X (0.2 g) were dissolved in 12 ml of water. The mixed solution was introduced to a 150 ml flask and uniformly agitated at isothermal condition for 20 min. Olefins (0.02 mol) was then added to the mixed solution. To start the reaction, chloroform (20 ml) was gradually added dropwise to complete the reaction in 30 min. Mono-dichlorocyclopropane and bis-dichlorocyclopropane were produced from the solution. After reaction, the solution was separated and the portion of organic solution was extracted by ether twice. Magnesium sulfate was also added to adsorb the residual water. Organic solvent (chloroform) and other residues were stripped in a vacuum evaporator. Chromatography method was employed to separate mono-dichlorocyclopropane and bis-dichlorocyclopropane products through an adsorption column (75 cm glass tube filled with 70–230 mesh silica gel powder, eluent: *n*-hexane). The mono-dichlorocyclopropane and bis-dichlorocyclopropane products were collected from the sample cell and concentrated by vacuum evaporation. Products of mono-dichlorocyclopropane and bis-dichlorocyclopropane of 98% purity were obtained. The products and the reactant were identified by GC-mass for molecular weight, FTIR and NMR (^1H NMR and ^{13}C NMR) for functional groups and elements for components. The contents of the components obtained from experiments are consistent with the theoretical values.

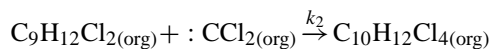
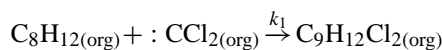
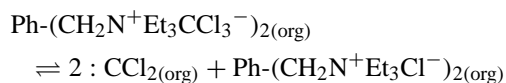
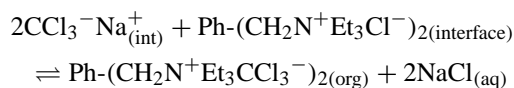
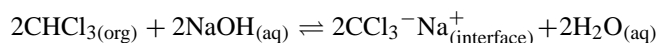
2.2.3. Kinetics of dichlorocyclopropanation in two-phase solution

The reactor was a 150 ml three-necked Pyrex flask, used for agitating the solution, inserting the thermometer, taking samples, and feeding the feed. A known quantity of NaOH (15 ml, 50%, w/w) was prepared. Known quantities of 4-vinyl-2-cyclohexene (reactant), 1,4-bis(triethylmethylammonium)benzene dichloride (catalyst), nonane (internal standard, 1 g) were then dissolved in chloroform (30 ml) to form the organic solution. To start the reaction, the aqueous and organic solutions were mixed in a 150 ml flask immersed in an isothermal water bath. The organic-phase sample (0.05 ml) was withdrawn from the reactor at each time interval, and put into test tubes containing 3 ml of dichloromethane. The content of product and reactant were measured by gas chromatography. The analysis conditions were: Shimadzu GC17A, J&W Scientific Inc., capillary column (db-1 column), 100%

poly(dimethylsiloxane) stationary phase, 15 m \times 0.525 mm column dimensions, carrier gas: nitrogen (60 ml/min), FID detector, 250 °C injection temperature.

3. Reaction mechanism and kinetic model

Trichloromethyl anion (CCl_3^-), which can convert to dichlorocarbene ($:\text{CCl}_2$), is generated from chloroform in the presence of alkaline solution. However, the organic olefin does not react with dichlorocarbene to form dichlorocyclopropane product because of easy hydrolysis of dichlorocarbene. Therefore, the addition of phase transfer catalyst (e.g., quaternary ammonium salt, QX) to the aqueous solution to generate dichlorocarbene in the organic solution is essential. An intermediate (Q^+CCl_3^-) is formed from the reaction of trichloromethyl anion and quaternary ammonium salt at the interface of two phases. This intermediate then transfers to the organic phase preparing for reaction with olefins to produce the product. The reaction mechanism is thus proposed as



where k_1 represents the intrinsic rate constant for the reaction of dichlorocarbene ($:\text{CCl}_2$) and 4-vinyl-1-cyclohexene (C_8H_{12}) to produce mono-dichlorocyclopropane ($\text{C}_9\text{H}_{12}\text{Cl}_2$) in the organic solution; and k_2 the intrinsic rate constant for the reaction of mono-dichlorocyclopropane ($\text{C}_9\text{H}_{12}\text{Cl}_2$) and dichlorocarbene ($:\text{CCl}_2$) to produce bis-dichlorocyclopropane ($\text{C}_{10}\text{H}_{12}\text{Cl}_4$) in the organic solution. For this, the change rate of 4-vinyl-1-cyclohexene due to reaction is expressed as

$$-\frac{d[\text{C}_8\text{H}_{12}]_o}{dt} = k_1[\text{C}_8\text{H}_{12}]_o[: \text{CCl}_2]_o \quad (1)$$

Dichlorocarbene was not detectable during the experimental steps. However, the concentration of dichlorocarbene was kept at a constant throughout the reaction. Thus, Eq. (1) can be rewritten as

$$-\frac{d[\text{C}_8\text{H}_{12}]_o}{dt} = k_{\text{app},1}[\text{C}_8\text{H}_{12}]_o \quad (2)$$

where

$$k_{\text{app},1} = k_1[: \text{CCl}_2]_o \quad (3)$$

Similarly, we obtain

$$k_{\text{app},2} = k_2[: \text{CCl}_2]_o \quad (4)$$

Therefore, the series reaction of 4-vinyl-1-cyclohexene and dichlorocarbene is irreversible and is expressed as,



As shown in Eq. (5), the change rates of these three components are:

$$\frac{d[\text{C}_8\text{H}_{12}]_o}{dt} = -k_{\text{app},1}[\text{C}_8\text{H}_{12}]_o \quad (6)$$

$$\frac{d[\text{C}_9\text{H}_{12}\text{Cl}_2]_o}{dt} = k_{\text{app},1}[\text{C}_8\text{H}_{12}]_o - k_{\text{app},2}[\text{C}_9\text{H}_{12}\text{Cl}_2]_o \quad (7)$$

$$\frac{d[\text{C}_{10}\text{H}_{12}\text{Cl}_4]_o}{dt} = k_{\text{app},2}[\text{C}_9\text{H}_{12}\text{Cl}_2]_o \quad (8)$$

Eq. (6) is integrated as

$$[\text{C}_8\text{H}_{12}]_o = [\text{C}_8\text{H}_{12}]_{o,i} \exp(-k_{\text{app},1}t) \quad (9)$$

where $[\text{C}_8\text{H}_{12}]_{o,i}$ is the initial concentration of 4-vinyl-1-cyclohexene. Define the conversion of 4-vinyl-1-cyclohexene, X as,

$$X = 1 - \frac{[\text{C}_8\text{H}_{12}]_o}{[\text{C}_8\text{H}_{12}]_{o,i}} \quad (10)$$

Thus, Eq. (9) can be expressed as,

$$-\ln(1 - X) = k_{\text{app},1}t \quad (11)$$

The value of $k_{\text{app},1}$ can be obtained by plotting the experimental data of $-\ln(1 - X)$ versus time. Substituting Eq. (9) into Eq. (7), we obtain the concentration of mono-dichlorocyclopropane, i.e.,

$$[\text{C}_9\text{H}_{12}\text{Cl}_2]_o = [\text{C}_8\text{H}_{12}]_{o,i} \frac{k_{\text{app},1}}{k_{\text{app},2} - k_{\text{app},1}} \\ \times \{\exp(-k_{\text{app},1}t) - \exp(-k_{\text{app},2}t)\} \quad (12)$$

The value of $k_{\text{app},2}$ can be estimated from the experimental data of mono-dichlorocyclopropane and from the knowledge of $k_{\text{app},1}$ -value given in Eq. (11) via parameter estimation.

4. Results and discussion

The purpose of this work is to study the reaction of 4-vinyl-1-cyclohexene in an alkaline solution/chloroform two-phase medium to synthesize mono-dichloro-cyclopropane (7,7-dichloro-3-vinyl-bicyclo[4.1.0]heptane) and bis-dichlorocyclopropane (7,7-dichloro-3-(2,2-dichloro-cyclopropyl)-bicyclo[4.1.0]heptane). Dichlorocarbene, which is produced from chloroform in the presence of alkali compound, reacts 4-vinyl-1-cyclohexene to produce these two additional products. The experimental results show a material balance between reactant and products, i.e., the consumption of the amount of reactant (4-vinyl-1-cyclohexene) equals to the sum of the generation of the amount of mono-dichlorocyclopropane and bis-dichlorocyclopropane products. No byproducts were observed during or after reaction.

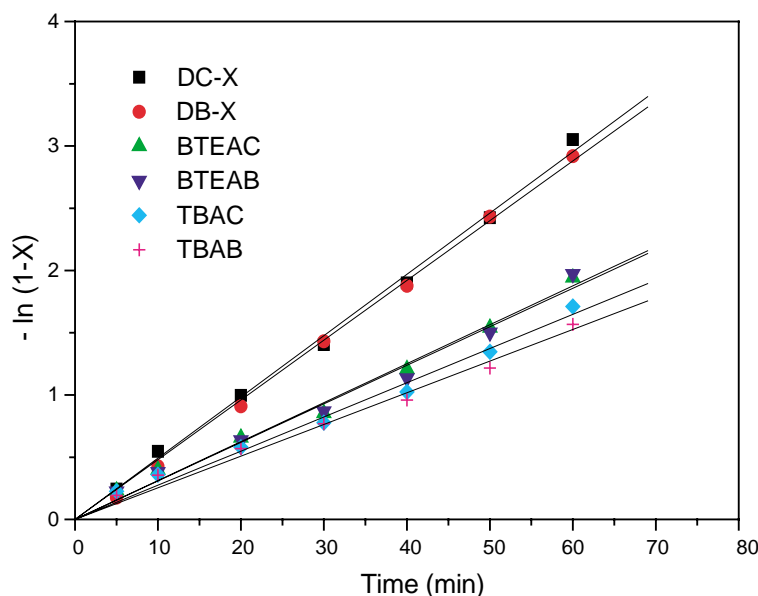


Fig. 1. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with different catalysts; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 0.1 mmol of catalyst, 20 °C, 800 rpm.

Furthermore, the mono-dichlorocyclopropane product first appeared, then followed by the bis-dichlorocyclopropane product. In the absence of phase transfer catalyst, neither mono-dichlorocyclopropane nor bis-dichlorocyclopropane was produced from the reaction of chloroform and sodium hydroxide solution for 2 h. The main reason is that dichlorocarbene, which is produced from the reaction of chloroform and sodium hydroxide, can be easily to be hydrolyzed in aqueous solution. Under this situation, no dichlorocarbene can react with 4-vinyl-1-cyclohexene to produce the desired products. However, the reaction is dramatically enhanced by adding a small amount of catalyst. This result confirms that two organic-phase reactions are in series.

4.1. Effect of catalysts

In this work, the newly synthesized 1,4-bis(triethylmethylammonium)benzene dichloride DC-X and 1,4-bis(triethylmethylammonium)benzene dibromide DB-X was employed as the phase transfer catalyst and its reactivity was compared with those of the conventional quaternary ammonium salts, such as BTEAC, BTEAB, TBAC and TBAB. The results are given in Fig. 1. The reaction follows a pseudo-first-order rate law. It is obvious that the catalytic activity of DC-X

or DB-X is much better than that of BTEAC or TBAB as catalyst in dichlorocyclopropanation. Two phenomena were observed from the experiments, i.e., the phase transfer catalyst of multisite activities possesses a higher reactivity than that of single-site activity; and the reactivity of BTEAC is greater than that of TBAB in dichlorocyclopropanation. This evidence is quite different from the extraction mechanism proposed by Starks [1]. Therefore, an interfacial reaction mechanism is proposed to explain the synthesis of dichlorocyclopropane in this work. In applying Eqs. (11) and (12), the apparent rate constants, $k_{\text{app},1}$ and $k_{\text{app},2}$ for using these catalysts (DC-X) and (DB-X), and quaternary ammonium salts (BTEAC, BTEAB, TBAC and TBAB) are given in Table 1. The value of $k_{\text{app},1}$ is larger than that of $k_{\text{app},2}$. Thus, two dichlorocyclopropanes were produced from the reaction solution during or after reaction.

4.2. Effect of agitation speed

The necessary condition for a reaction to occur is the effective collision of reactant molecules, even in the phase transfer catalysis system. In the two-phase reaction system, the effect of agitation speed on the extraction mechanism (Starks) and interfacial reaction mechanism (Makosza) are

Table 1

Effect of the new catalyst (DC-X and DB-X), and quaternary ammonium salts (BTEAC, BTEAB, TBAC and TBAB) on the apparent rate constants, $k_{\text{app},1}$ and $k_{\text{app},2}$; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% NaOH , 0.1 mmol of catalyst, 20 °C, 800 rpm

	Catalysts					
	DC-X	DC-B	BTEAC	BTEAB	TBAC	TBAB
$k_{\text{app},1} \times 10^{-2} \text{ (min}^{-1}\text{)}$	4.92	4.80	3.13	3.09	2.75	2.54
$k_{\text{app},2} \times 10^{-2} \text{ (min}^{-1}\text{)}$	0.717	0.641	0.486	0.426	0.400	0.368

Table 2

Effect of the agitation speed on the apparent rate constants, $k_{app,1}$ and $k_{app,2}$; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% NaOH, 0.1 mmol of DC-X catalyst, 20 °C

	Agitation speed (rpm)				
	200	400	600	800	1000
$k_{app,1} \times 10^{-2}$ (min ⁻¹)	0.113	0.793	2.92	4.92	7.42
$k_{app,2} \times 10^{-2}$ (min ⁻¹)	–	0.131	0.387	0.717	1.128

quite different. For an extraction mechanism reaction system, the reaction rate is no longer increases with the increase in agitation speed above 300 rpm. However, the reaction rate further increases with the increase in agitation speed even when it is greater than 1000 rpm. The main reason is that the two-phase interfacial mass transfer area, which can influence the reaction rate, also increases with the increase in agitation speed. The effect of agitation speed on the conversion of 4-vinyl-1-cyclohexene is given in Fig. 2 and Table 2. Here again, the reaction follows a pseudo-first-order rate law. Moreover, the conversion increases with the increase in the agitation speed up to 1000 rpm, which agrees with the interfacial reaction mechanism rather than Starks' extraction mechanism.

4.3. Effect of temperature

The present work is to investigate the reaction of 4-vinyl-1-cyclohexene and chloroform catalyzed by a new catalyst DC-X in the presence of alkaline solution under various reaction temperatures from 20 to 35 °C. The results are given in Fig. 3. As expected, the reaction rate increases with the increase in the temperature. Moreover, the reaction follows a pseudo-first-order rate law. As shown in Fig. 4,

where the apparent rate constants $k_{app,1}$ and $k_{app,2}$ are plotted versus $1/T$, the activated energies obtained are $E_{a,1} = 8.78$ kcal/mol and $E_{a,2} = 6.18$ kcal/mol, respectively.

4.4. Effect of alkaline concentration

The dichlorocyclopropanation is highly dependent on the alkali compound. Dichlorocarbene (:CCl₂) which can be generated from chloroform in the presence of alkaline solution, reacts with organic-phase reactant (e.g., 4-vinyl-1-cyclohexene) to produce the desired products. Therefore, the rate of dichlorocyclopropanation is highly influenced by the concentration of alkali in aqueous solution. Sodium hydroxide, potassium hydroxide and sodium bicarbonate are the common alkali compounds. However, NaOH is frequently used as the reagent because of its low cost, high effectiveness and separation factor. The results of conversion of 4-vinyl-1-cyclohexene via dichlorocyclopropanation using NaOH as the alkaline compound are given in Fig. 5. It is obvious that the conversion is highly dependent on the concentration of alkali in the aqueous solution. The conversion increases with the increase in concentration of alkaline. The reaction also follows a pseudo-first-order rate law.

In the absence of phase transfer catalyst, the generated dichlorocarbene can be easily hydrolyzed [17,18], i.e.,

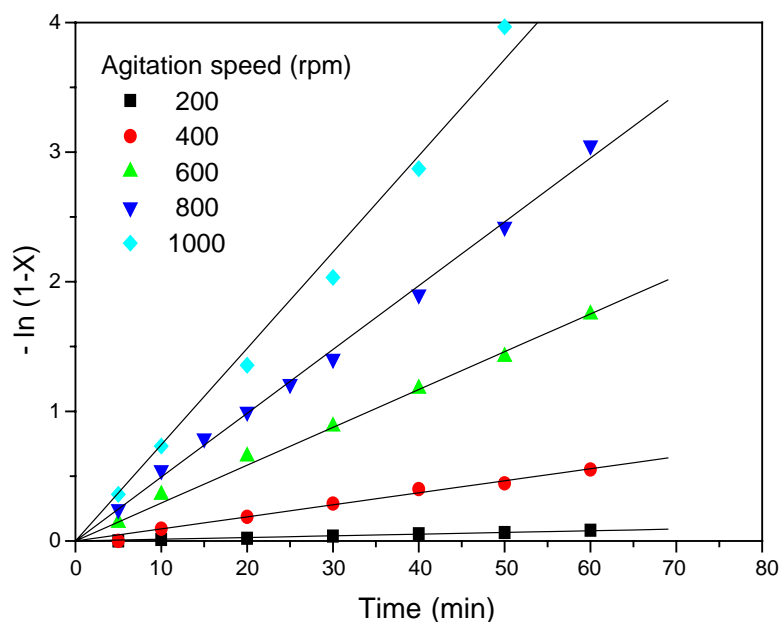
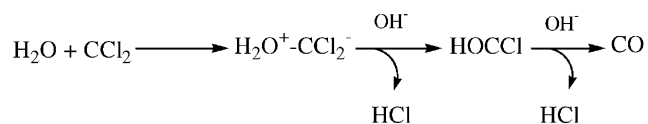
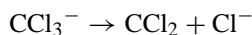
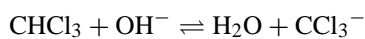


Fig. 2. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with various agitation speeds; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% NaOH_(aq), 0.1 mmol of DC-X, 20 °C.

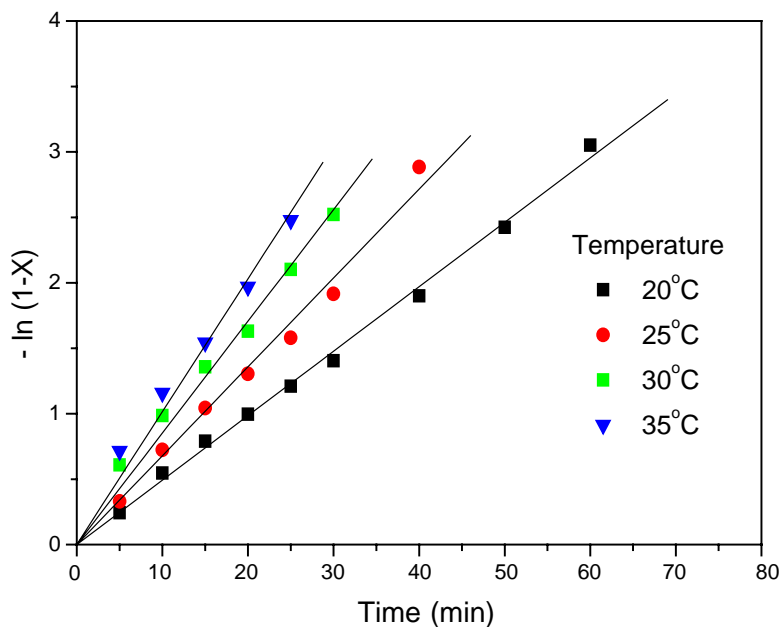


Fig. 3. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with various reaction temperatures; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 0.1 mmol of DC-X, 800 rpm.

It is thus obvious that hydroxide ions (OH^-) in the aqueous phase also affect the degree of hydrolyzing $:\text{CCl}_2$. Experimental results indicate that the reaction rate is slow at low alkaline concentration. However, the reaction is dramatically enhanced when the concentration of alkaline is increased. The results are depicted in Fig. 6. However, the result obtained for using 100–250 mmol of NaOH is similar to that of Solaro et al. [19] in the ethylation of phenylacetonitrile catalyzed by TBAB catalyst, and Balakrishnan et al. [20] in

using BTEAC to initiate the dichlorocyclopropanation of styrene.

The main reason is that the hydration of OH^- is minimized and the activity of OH^- is increased by increasing the concentration of alkaline. For such, the hydrolysis of dichlorocarbene is also minimized. Therefore, the reaction of dichlorocyclopropanation at higher alkaline concentration of NaOH is much larger than that at low alkaline concentration of NaOH .

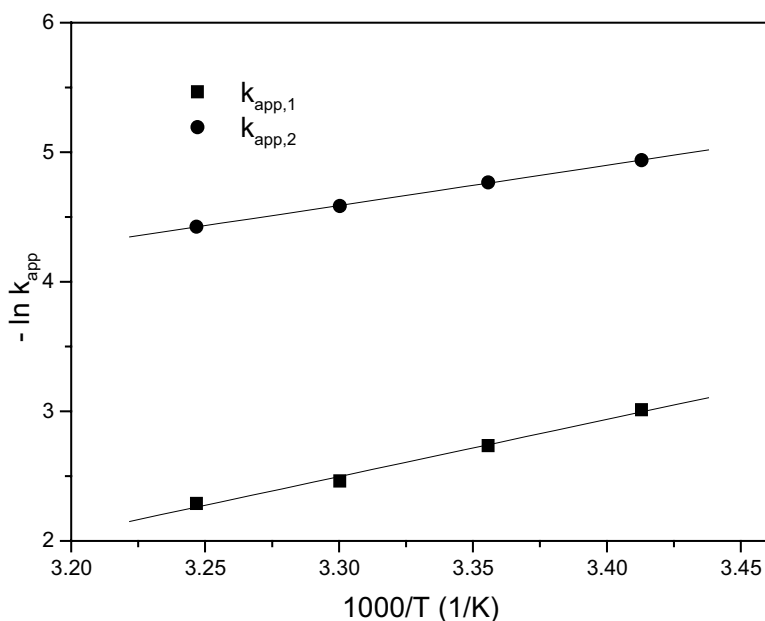


Fig. 4. A plot of apparent rate constants vs. various reaction temperatures; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 0.1 mmol of DC-X, 800 rpm.

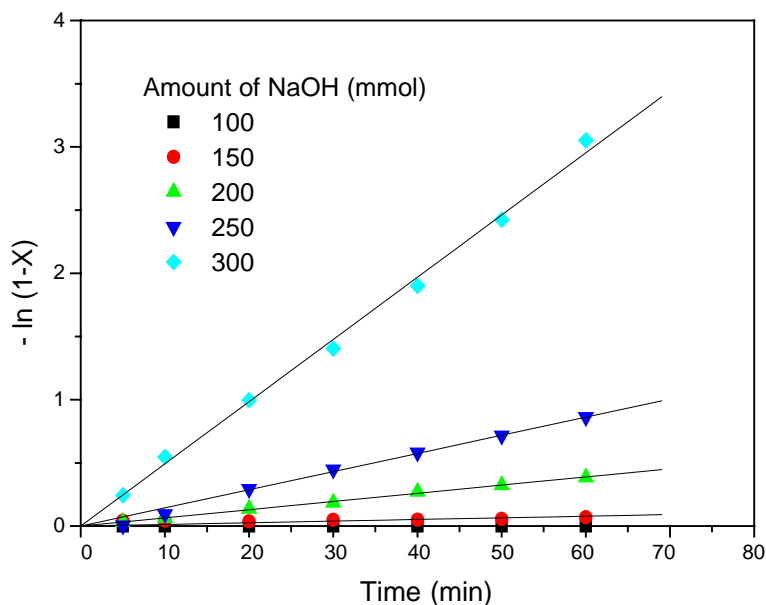


Fig. 5. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with various amounts of NaOH; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 12 ml of H_2O , 20°C , 800 rpm.

4.5. Effect of amount of catalyst DC-X

In this work, the effect of the amount of DC-X catalyst on the conversion of 4-vinyl-1-cyclohexene is investigated. The results for using 0–3 mol% of DC-X catalyst (relative to reactant) are shown in Fig. 7. In the absence of DC-X catalyst, no reaction of dichlorocyclopropanation is observed. However, the reaction is greatly enhanced by adding a small quantity of DC-X catalyst. As seen in the experimental results, the reaction rate is increased with the

increase in the amount of DC-X catalyst up to 1.51 mol%. The reason is that the opportunity of collision between $\text{Na}^+\text{CCl}_3(\text{interface})^-$ and $\text{Ph}-(\text{CH}_2\text{N}^+\text{Et}_3\text{Cl}^-)_2(\text{interface})$ is increased by increasing DC-X catalyst concentration. Therefore, the opportunity of forming a complex between $\text{Ph}-(\text{CH}_2\text{N}^+\text{Et}_3\text{Cl}^-)_2(\text{org})$ and dichlorocarbene is largely increased, i.e., the concentration of dichlorocarbene in the organic phase is enhanced. Hence, the apparent rate constant is increased with the increase in the amount of DC-X catalyst.

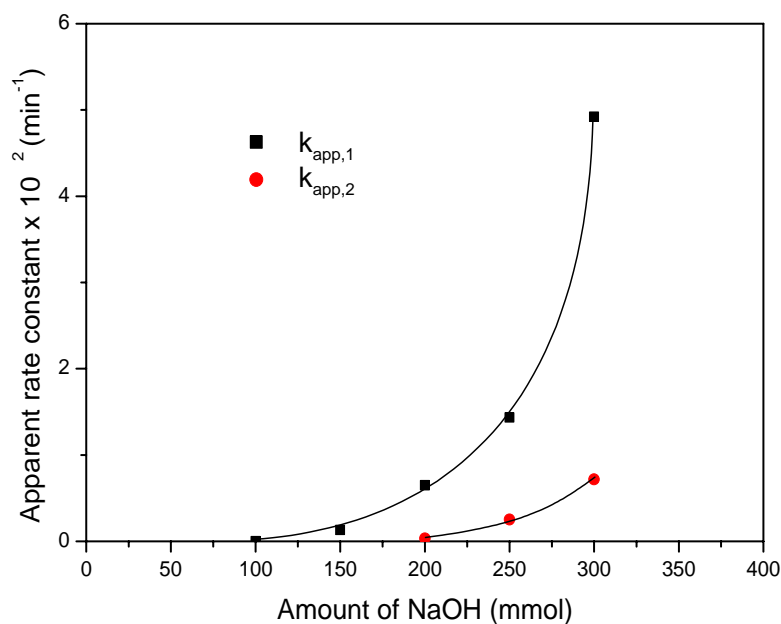


Fig. 6. A plot of apparent rate constants vs. various amounts of NaOH; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 12 ml of H_2O , 20°C , 800 rpm.

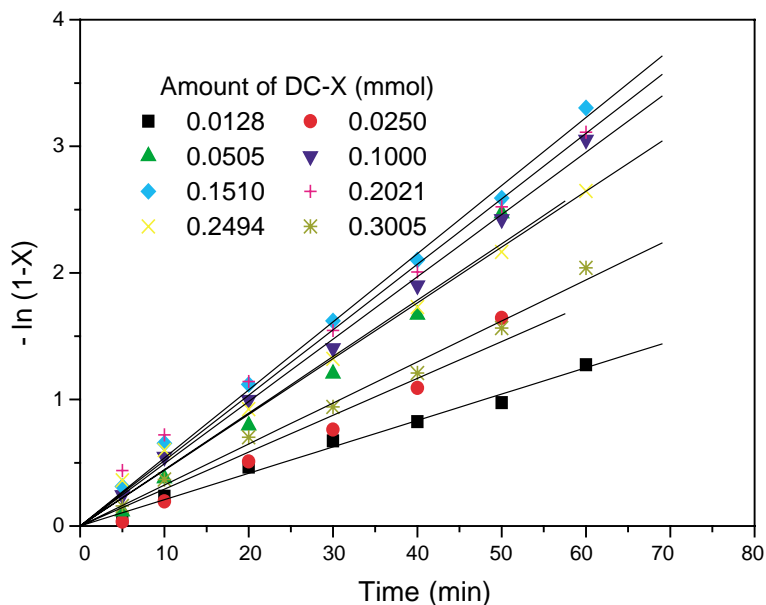


Fig. 7. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with various amounts of DC-X catalyst; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 20°C , 800 rpm.

However, as shown in Figs. 7 and 8, the reaction rate is then decreased for further increasing the amount of DC-X catalyst from 1.51 to 3 mol%. It is probably because the reaction is more influenced by the interfacial concentration of DC-X at the interface rather than in the bulk organic-phase solution. The formation of $\text{Ph}-(\text{CH}_2\text{N}^+\text{Et}_3\text{CCl}_3^-)_{2(\text{org})}$ from DC-X and dichlorocarbene at the interface such that the concentration of dichlorocarbene in the bulk organic-phase solution is decreased. Thus, the apparent rate constants are reduced for further increasing the amount of DC-X catalyst.

4.6. Effect of amount of 4-vinyl-1-cyclohexene (reactant)

The effect of the amount of 4-vinyl-1-cyclohexene on the conversion of 4-vinyl-1-cyclohexene is shown in Fig. 9. It is shown that the reaction rate is highly dependent on the amount of 4-vinyl-1-cyclohexene in which the mass transfer and the reaction rate is decreased with the increase in the amount of 4-vinyl-1-cyclohexene. This result is similar to the dichlorocyclopropanation of 1,7-octadiene catalyzed by benzyltriethylammonium (BTEAC) catalyst

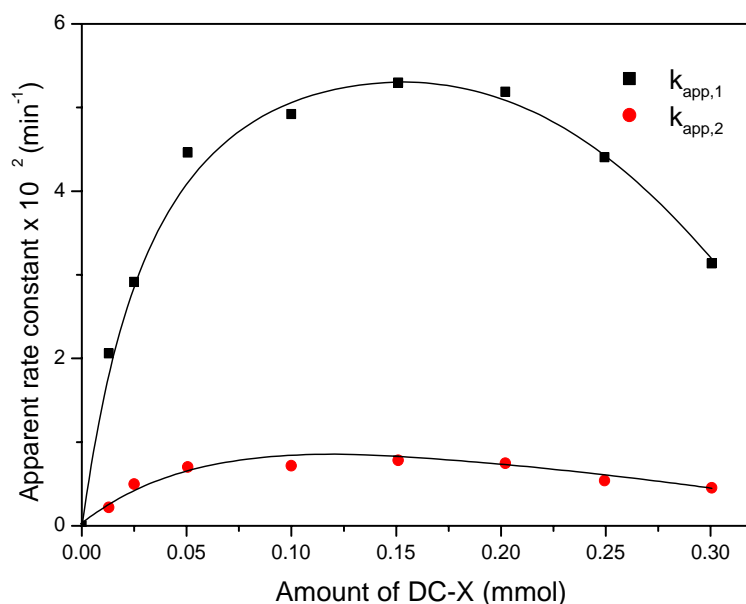


Fig. 8. A plot of apparent rate constant vs. various amounts of DC-X catalyst; 10 mmol of 4-vinyl-1-cyclohexene, 30 ml of chloroform, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 20°C , 800 rpm.

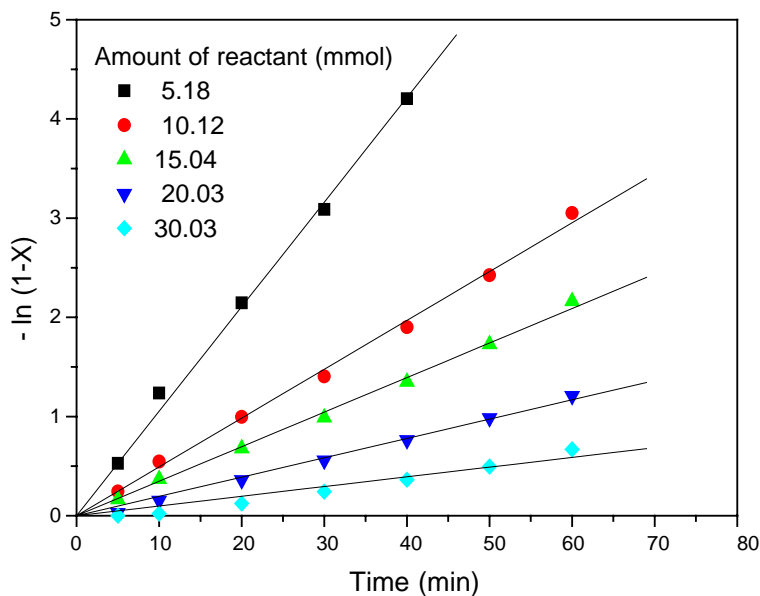


Fig. 9. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with various amounts of 4-vinyl-1-cyclohexene; 30 ml of chloroform, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 0.1 mmol of DC-X, 20°C, 800rpm.

and the dichlorocyclopropanation of 1-octene catalyzed by 3-(*N,N*-trialkylammonio)propan sulfonate. The reason is that the amount of active-site catalysts is kept constant value when using a fixed amount of catalysts. Because the amount of organic-phase reactant is increased, the molar ratio of the active-site catalyst over the reactant is thus decreased.

The corresponding $k_{\text{app},1}$ and $k_{\text{app},2}$ for various amounts of 4-vinyl-1-cyclohexene are given in Table 3. It is obvious that low 4-vinyl-1-cyclohexene favors the occurrence of reaction.

4.7. Effect of volume of organic solvents

In this study, chloroform is used as the organic solvent and the source of generating dichlorocarbene. Chloroform is converted to dichlorocarbene in the presence of alkali compound and reacts with 4-vinyl-1-cyclohexene of limited quantity in the organic phase to produce the desired products. The results are given in Fig. 10. As can be seen, the reaction follows a pseudo-first-order rate law. The reaction rate is decreased with the increase in the volume of chloroform. The

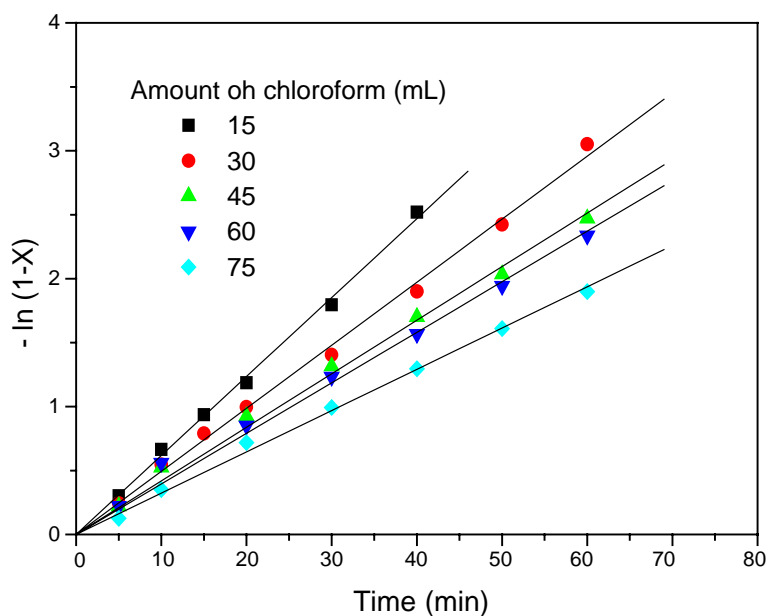


Fig. 10. A plot of $-\ln(1-X)$ of 4-vinyl-1-cyclohexene vs. time with various amounts of chloroform; 10 mmol 4-vinyl-1-cyclohexene, 15 ml of 50% $\text{NaOH}_{(\text{aq})}$, 0.1 mmol of DC-X, 20°C, 800rpm.

Table 3

Effect of the amount of 4-vinyl-1-cyclohexene on the apparent rate constants, $k_{app,1}$ and $k_{app,2}$; 30 mmol of chloroform, 15 ml of 50% NaOH, 0.1 mmol of DC-X catalyst, 20 °C, 800 rpm

Reactant (mmol)	$k_{app,1} \times 10^{-2}$ (min ⁻¹)	$k_{app,2} \times 10^{-2}$ (min ⁻¹)	Reactant/catalyst
5.18	10.53	1.041	51.8
10.12	4.92	0.717	101.1
15.04	3.48	0.528	137.7
20.03	1.95	0.191	200.3
30.03	0.98	–	300.3

Table 4

Effect of the volume of chloroform on the apparent rate constants, $k_{app,1}$ and $k_{app,2}$; 10 mmol of 4-vinyl-1-cyclohexene, 15 ml of 50% NaOH, 0.1 mmol of DC-X catalyst, 20 °C, 800 rpm

	Chloroform (ml)				
	15	30	45	60	75
$k_{app,1} \times 10^{-2}$ (min ⁻¹)	6.17	4.92	4.19	3.95	3.23
$k_{app,2} \times 10^{-2}$ (min ⁻¹)	0.934	0.717	0.602	0.506	0.392

reason is that the concentration of dichlorocarbene generated is decreased with the increase in the amount of chloroform. The collision of dichlorocarbene and 4-vinyl-1-cyclohexene is thus decreased. The corresponding $k_{app,1}$ and $k_{app,2}$, which are functions of the value of chloroform, are shown in Table 4. Both $k_{app,1}$ and $k_{app,2}$ are decreased with the increase in the volume of chloroform, as expected.

5. Conclusion

In this work, a high yield of product and a high reaction rate from the dichlorocyclopropanation of 4-vinyl-1-cyclohexene were obtained from the reaction of 4-vinyl-1-cyclohexene and chloroform in an alkaline solution/chloroform two-phase medium catalyzed by a novel phase transfer catalyst, 1,4-bis(triethylmethylammonium)benzene dichloride (DC-X). This two-site activity phase transfer catalyst exhibits higher reactivity than the conventional BTEAC, BTEAB, TBAC and TBAB catalysts. According to the experimental evidence, the reaction follows an interfacial reaction mechanism, in which the reaction rate is highly dependent on the agitation speed up to 1000 rpm. An optimum reaction rate is obtained using a 1.55 mol% of DC-X catalyst. The conversion of 4-vinyl-1-cyclohexene decreases with the increase in the amount of 4-vinyl-1-cyclohexene and chloroform. The reason is that both the molar ratio of catalyst to 4-vinyl-1-cyclohexene and the concentration of dichlorocarbene are decreased with the increase in the amount of chloroform and 4-vinyl-1-cyclohexene. However, the reaction rate increases with the increase in the amount of catalyst and alkaline concentration. The reason is that Ph-(CH₂N⁺Et₃CCl₃⁻)_{2(org)} produced when more catalysts are added. Hence, the amount of dichlorocarbene in the organic phase is decreased, thus reducing the reaction rate.

Acknowledgements

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